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Subtle metastability of the layered magnetic topological insulator MnBi_2Te_4 from weak interactions

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Layered quantum materials can host interesting properties, including magnetic and topological, for which enormous computational predictions have been done. Their thermodynamic stability is much less visited computationally, which however determines the existence of materials and can be used to guide experimental synthesis. MnBi_2Te_4 is one of such layered quantum materials that was predicted to be an intrinsic antiferromagnetic topological insulator, and later experimentally realized but in a thermodynamically metastable state. Here, using a combined first-principles-based approach that considers lattice, charge, and spin degrees of freedom, we investigate the metastability of MnBi_2Te_4 by calculating the Helmholtz free energy for the reaction $\text{Bi}_2\text{Te}_3 + \text{MnTe} \rightarrow \text{MnBi}_2\text{Te}_4$. We identify a temperature range (~ 500 – 873 K) in which the compound is stable with respect to the competing binary phases, consistent with experimental observation. We validate the predictions by comparing the calculated specific heats contributed from different degrees of freedom with experimental results. Our findings indicate that the degrees of freedom responsible for the van der Waals interaction, lattice vibration, magnetic coupling, and nontrivial band topology in MnBi_2Te_4 not only enable emergent phenomena but also play a crucial role in determining its thermodynamic stability. This conclusion lays the foundation for the future computational material synthesis of novel layered systems.

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INTRODUCTION

Layered quantum materials, such as graphene and two-dimensional (2D) semiconductors of transition metal dichalcogenides, have revolutionized many fields in condensed matter physics and materials science because of their exotic quantum properties¹. A new member in this family is MnBi_2Te_4 that is an intrinsic antiferromagnetic topological insulator (TI) currently under intensive study^{2–10}. In MnBi_2Te_4 , the interplay between magnetism and topology has been shown to generate exotic quantum states, including quantum anomalous Hall effect⁴, axion insulator^{6,7}, and high-Chern-number insulator⁹, upon exfoliation to atomically thin layers.

MnBi_2Te_4 is formed by intercalating magnetic MnTe layers into the quintuple layers of Bi_2Te_3 , which is topologically protected due to spin–orbit coupling (SOC)-induced band inversions^{11,12}. The experimental synthesis of large, pure, high-quality MnBi_2Te_4 single crystals suitable for magnetotransport measurements is however notoriously difficult. Different experiments have confirmed that MnBi_2Te_4 is a metastable phase that can only be synthesized within a narrow temperature range below 873 K^{3,13–15}. Without a fundamental understanding of its metastability, the ideal growth conditions for pure, large crystal synthesis will remain elusive, ultimately preventing further experimental study of its unique topological and magnetotransport properties. Furthermore, although there have been a significant number of materials predicted to host interesting topological properties^{16–18}, using different symmetry indicators^{16–19}, there are only a handful of experimental realizations of such predictions^{16–18,20}. Hence, the understanding of the metastability of MnBi_2Te_4 is also highly desirable for the synthesis of other candidate layered topological materials.

Thermodynamic stability of materials can be predicted from chemical reaction free energy based on first-principles density functional theory (DFT) calculations. Nevertheless, for complex layered magnetic quantum materials like MnBi_2Te_4 , such predictions are challenging, due to the increasing importance of various weak interactions (including SOC, magnetic coupling, lattice vibrations, and vdW interactions), most of which are also responsible for their emergent properties, as illustrated in Fig. 1. Typically, these materials have different kinds of chemical bonds ranging from strong intralayer covalent bonds to weak interlayer vdW interactions, with interaction strengths across almost 3 orders of magnitude (from ~ 1 eV for strong bonds to ~ 1 meV for vdW interactions). Both strong chemical bonds and weak interactions are equally important for the thermodynamic stability predictions, demanding a single density functional approximation for simultaneously accurate descriptions. More importantly, the electronic, magnetic, and vibrational thermal excitation energies of these materials at finite temperature can be up to several tens of meV; although this scale is typically negligible for stability predictions of bulk solids²¹, it is comparable to the thermal energy required to stabilize MnBi_2Te_4 . Since DFT is a zero-temperature ground-state electronic structure method, post-DFT models have to be used to describe such excitations. Therefore, all these interactions have to be considered and described accurately for the thermodynamic stability of MnBi_2Te_4 , either at the DFT level or by DFT-based models.

Here, using a set of first-principles-based approaches that consider lattice, charge, and spin degrees of freedom to take into account the various weak interactions, we calculate the temperature-dependent reaction free energy of MnBi_2Te_4 based on the reaction $\text{MnTe} + \text{Bi}_2\text{Te}_3 \rightarrow \text{MnBi}_2\text{Te}_4$, which identifies a narrow temperature range for the metastability of MnBi_2Te_4 .

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Fig. 1 Schematic of synthesis reaction and various interactions determining metastability in MnBi_2Te_4 . **a** Schematic of the synthesis reaction of the target ternary layered magnetic material MnBi_2Te_4 from two competing binary phases: $\text{Bi}_2\text{Te}_3 + \text{MnTe} \rightarrow \text{MnBi}_2\text{Te}_4$. Note the layered structures of Bi_2Te_3 and MnBi_2Te_4 , and the localized magnetic moments (illustrated by blue and red arrows on Mn) in MnTe and MnBi_2Te_4 . **b** Schematic of the weak interactions considered here, found to be critical in determining the metastability of MnBi_2Te_4 . Top left: SOC; top right: magnetic coupling interaction; bottom left: anharmonic nature of lattice vibration in comparison with the harmonic approximation; bottom right: vdW interaction.

consistent with experiments. These approaches are then validated by comparing the predicted specific heat capacities of the relevant compounds to experimental results.

Figure 2 shows that MnBi_2Te_4 is unstable with respect to its competing binary phases (MnTe and Bi_2Te_3) for low temperatures, and becomes stable above 500 K, indicated by the calculated reaction free energy (blue solid line) with contributions from all considered degrees of freedom. The predicted thermodynamic equilibrium temperature $T = 500$ K is close to the experimentally estimated formation temperature range between 673¹⁴ and 808 K¹³ and above ~423 K, at which MnBi_2Te_4 was observed to start decomposing during heating¹³. Since the melting points are ~853 and ~873 K for Bi_2Te_3 and MnBi_2Te_4 , respectively¹⁴, the quenching required for single crystal synthesis of MnBi_2Te_4 without the minor Bi_2Te_3 phase must occur between ~853 and ~873 K. This narrow temperature window, in addition to the fact that MnBi_2Te_4 is only more stable than the competing binaries by ~6 meV/atom in this window, explains why previous experimental attempts at synthesizing large single crystals have been difficult¹⁴.

Below, we decompose the contributions from various weak interactions to the metastability of MnBi_2Te_4 . Figure 2 shows that vdW, SOC, lattice vibration, and magnetic coupling stabilize MnBi_2Te_4 with respect to the competing binaries on average by ~11, ~2.5, ~5, and ~5 meV/atom, respectively, while the electronic thermal excitation is negligible. This suggests that SOC, vdW, magnetic coupling, and lattice vibrations play equally important roles in determining this compound's metastability accurately with temperature, given that MnBi_2Te_4 is only more stable than

Fig. 2 Reaction free energy based on $\text{Bi}_2\text{Te}_3 + \text{MnTe} \rightarrow \text{MnBi}_2\text{Te}_4$. The energy is calculated at different levels of theory, including the 0 K DFT reaction energy from PBE (E_{PBE}), SCAN + rVV10 ($E_{\text{SCAN+rVV10}}$), and SCAN + rVV10 with SOC ($E_{\text{SCAN+rVV10+SOC}}$, denoted as E_0); the electronic excitation (el), lattice vibrational (harmonic approximation, ph_{HA} , and quasi-harmonic approximation with Debye model to include the anharmonic contribution for high temperature starting around 150 K, ph_{AHA}), and magnetic (mag) contributions. Experimental melting temperatures of Bi_2Te_3 (T_{mBT}) and MnBi_2Te_4 (T_{mMBT}), MnBi_2Te_4 start decomposition temperature (T_{sd}) upon heating (dashed blue line)¹⁴, and uncertainty in MnBi_2Te_4 formation temperature (shaded area)^{13,14} are shown.

the competing binaries by about 6 meV/atom below the melting temperature from the calculations.

RESULTS AND DISCUSSION

Van der Waals interaction

It is well known that layered materials are bound by vdW interactions between layers, while the popular Perdew–Burke–Ernzerhof (PBE) density functional²² misses most vdW interactions and barely binds layered materials^{23,24}. Meanwhile, it has been shown that the strongly constrained and appropriately-normed (SCAN) density functional^{25,26} combined with the revised Vydrov–Van Voorhis (rVV10) nonlocal correlation density functional^{27,28} is effective in accurately describing structural and energetic properties of layered materials²⁴. As expected, Fig. 2 shows that PBE destabilizes MnBi_2Te_4 with respect to the competing binaries by about 11 meV/atom in comparison with SCAN + rVV10 for the 0 K ground-state energies. Since 11 meV/atom is comparable to the finite temperature contributions to the reaction free energy from the electronic, magnetic, and vibrational degrees of freedom, PBE will falsely predict that MnBi_2Te_4 cannot be synthesized below its melting temperature, even in a metastable phase. In addition to the vdW interaction, it is likely that SCAN + rVV10 more accurately describes the d electrons of Mn (and hence the magnetic properties of MnTe and MnBi_2Te_4) when compared to PBE, due to the reduced self-interaction errors, a result demonstrated by previous studies on many other transition metal compounds^{25,26,29–38}.

Spin–orbit coupling

It is usually assumed that SOC is a purely atomic effect and canceled out in a reaction free energy calculation²¹. Figure 2 shows that the inclusion of SOC stabilizes MnBi_2Te_4 with respect

to MnTe and Bi₂Te₃ by ~ 2.5 meV/atom, which is negligible for typical solid reactions but is substantial for the metastability of MnBi₂Te₄. It is well known that SOC becomes important for heavy atoms, like Bi and Te, and is responsible for the topological properties of Bi₂Te₃ and MnBi₂Te₄, while the open *d*-shell of Mn provides localized magnetic moments for MnTe and MnBi₂Te₄. The synergy of SOC- and AFM-ordered localized magnetic moments results in MnBi₂Te₄ being an intrinsic magnetic TI³⁹. Our results further suggest that the presence of the magnetic moments enhances the SOC to lower the total energies more for MnBi₂Te₄ and MnTe than for Bi₂Te₃ (see Supplementary Table 1).

Electronic contribution

Figure 2 shows that the electronic contribution to the reaction free energy is negligible. This is to be expected, since the relevant compounds are semiconductors with band gaps no less than 0.1 eV (see Supplementary Fig. 1), an energy level much larger than the electronic thermal excitations for the considered temperature range.

Vibrational contribution (harmonic approximation and anharmonicity)

Figure 2 shows that lattice vibrations under the harmonic approximation (HA) stabilize the ternary phase more than the competing binaries. This is because the MnTe binary is much stiffer than the other two compounds, as illustrated by their equations of state (see Supplementary Fig. 2), and thus has much fewer phonon modes at low frequencies in the computed phonon density of states (see Supplementary Fig. 3). We also found that the lattice anharmonicity modeled by the Quasi-harmonic Debye (QHA-Debye) model^{40,41} and the Slater approximation⁴¹ to the Debye temperature Θ_D stabilizes MnBi₂Te₄ with respect to MnTe and Bi₂Te₃. This is probably due to the fact that MnTe is stiffer in its equation of state and experiences less anharmonicity in the temperature range considered here than the other two compounds. The anharmonicity has an effect of softening the phonon modes and therefore likely reduces the phonon frequencies of MnBi₂Te₄ and Bi₂Te₃ more than MnTe, favoring thermal population. This effectively stabilizes MnBi₂Te₄ with respect to MnTe and Bi₂Te₃ as temperature increases.

Magnetic contribution

MnBi₂Te₄ has roughly the same Mn magnetic moment as MnTe, $\sim 4.3 \mu_B$ ⁴², while the exchange coupling strength J_{ij} is much weaker (see Supplementary Table 2 and Supplementary Fig. 4), likely due to the layered structure⁴³. Similar to the lattice vibration effect, the stronger magnetic coupling should result in higher frequency magnons that destabilize MnTe more than MnBi₂Te₄ as temperature increases, as illustrated in Fig. 2. We note for MnBi₂Te₄, our calculated J_{ij} are about twice of the experimental ones⁴³ in magnitude but with different signs. In view of the small energy scale of J_{ij} (in sub meV) of MnBi₂Te₄, this discrepancy can result from the remaining self-interaction errors in SCAN + rVV10^{25,26,32,33}, or from other error or uncertainty sources in experiments, for example defects in the sample as discussed in Supplementary materials. We would like to stress that our calculated specific heat of MnBi₂Te₄ combining contributions from all degrees of freedom (including the magnetic specific heat) matches well the experimental result to be discussed below, which is relevant to the thermodynamic stability.

Specific heat

To validate our calculations, we compare the experimental with the calculated heat capacity at constant pressure (C_p) of the ternary phase MnBi₂Te₄ and its competing binary phases Bi₂Te₃ and MnTe, as shown in Fig. 3. We choose to focus on C_p because it

Fig. 3 Calculated heat capacity from electronic, magnetic, and vibrational contributions, compared with available experimental data. **(a)** Bi₂Te₃^{71–73}. **(b)** MnTe^{74,75}. **(c)** MnBi₂Te₄¹⁴. C_{v_el} , C_{v_mag} , and $C_{v_ph_HA}$ are contributions from electronic, magnetic, and vibrational (HA) excitations calculated within the constant volume approximation at 0 K equilibrium volume. $C_{p_ph_AHA}$ is the constant pressure specific heat considered for high temperature above 150 K from quasi-harmonic approximation with the Debye model.

is closely related to the free energy and is the key quantity obtained from calorimetric measurements. Here, we neglect the thermal expansion effect on the electronic and magnetic contributions to C_p and thus use C_v for these two contributions instead. A complete description of the calculations is included in the computational methods section.

When compared to the most recent experimental data, our predictions are accurate for MnTe for the whole range of temperature where experimental data are available up to ~600 K and for Bi₂Te₃ up to ~400 K. For MnBi₂Te₄, our predicted specific heat is in good agreement with the experimental one up to ~200 K, which was measured on a single crystal sample of MnBi₂Te₄ we synthesized using the Bi–Te flux method. Moreover, for both MnTe ($T_N \approx 300$ K) and MnBi₂Te₄ ($T_N \approx 25$ K), we predict well-defined peaks in C_p near the respective antiferromagnetic phase transition temperatures, consistent with experimental data. Since heat capacity is closely related to the free energy, these results reinforce the reliability of our stability estimation for MnBi₂Te₄.

Notable discrepancies between the computed and experimental results for Bi₂Te₃ (see Fig. 3a) however occur above ~400 K. This is likely due to the formation of point defects at high temperatures, such as vacancies and antisite defects, which has been consistently observed in experiments¹⁴. Formation of similar defects were also observed in MnBi₂Te₄¹⁴, and thus similar discrepancies would be expected. However, C_p measurements of MnBi₂Te₄ are nearly impossible at temperatures above ~423 K, at which the thermal vibration is strong enough to drive MnBi₂Te₄ out of the metastable state and MnBi₂Te₄ was observed to start decomposing during heating¹³. The effects of defects in the total reaction free energy from Bi₂Te₃ and MnBi₂Te₄ can be canceled out largely.

In summary, we have computationally analyzed the metastability of the recent antiferromagnetic TI MnBi₂Te₄ and have successfully synthesized high-quality single crystals for specific heat measurements. Our DFT-based approach yields specific heat results in good agreement with experimental data, validating our stability estimation of MnBi₂Te₄ as a function of temperature. We confirm that MnBi₂Te₄ is a metastable phase in a short range of temperatures (~500–873 K) with a small reaction free energy less than ~6 meV/atom, explaining the previous difficulties confronted in experimental synthesis. We demonstrate that fundamental weak interactions, including SOC, vdW, magnetic coupling, and lattice vibrations all contribute to this subtle high-temperature metastability. This finding potentially facilitates future computational discoveries of novel stable or metastable 2D magnetic topological materials, as well as their defect-related properties^{44–46}.

METHODS

Experimental methods

Single crystals of MnBi₂Te₄ were synthesized using the Bi–Te flux method¹⁵. The starting materials of Mn, Bi, and Te powder were mixed with a molar ratio of 1:10:16 and loaded into an Al₂O₃ crucible, then sealed in a quartz tube under high vacuum. The mixture was heated to 1173.15 K in a muffle furnace and held there for 24 h to allow homogeneous melting, then slowly cooled down to 863.15 K at a rate of 3 K/h. After removing the excess Bi₂Te₃ flux through centrifuging, plate-like single crystals were obtained. Their crystal structure was confirmed by X-ray diffraction measurements, and their chemical composition was examined using energy dispersive X-ray spectroscopy. The specific heat of MnBi₂Te₄ up to 200 K was measured with an adiabatic relaxation technique using a commercial Physical Property Measurement System (Quantum Design). These data are plotted in Fig. 3c.

Computational methods

The DFT⁴⁷ calculations were carried out using the Vienna Ab-initio Simulation Package (VASP)⁴⁸ with the projector-augmented wave (PAW) method^{49,50}. The recently developed SCAN density functional^{25,26} was used for its superior performance in the description of different chemical bonds and transition metal compounds^{25,26,29–33}. A long-range vdW correction was combined with SCAN through the rVV10 nonlocal correlation²⁸, a revised form of VV10, the Vydrov–Van Voorhis nonlocal correlation functional²⁷. The PAW method was employed to treat the core ion–electron interaction. An energy cutoff of 520 eV was used to truncate the

plane wave basis. We used Γ -centered meshes with a spacing threshold of 0.15 Å^{−1} for K-space sampling. Geometries of the three compounds were allowed to relax until the maximum ionic forces were below a threshold of 1 meV Å^{−1}. We used the Phonopy code⁵¹ to obtain the harmonic force constants from VASP atomic force calculations within finite displacement method (0.03 Å), key information for phonon frequency ω_q (where q is the wave vector) calculations.

The key quantity for thermodynamic stability predictions of solids is the Helmholtz free energy, defined as

$$F(V, T) = E_0(V) + F^{\text{el}}(V, T) + F^{\text{vib}}(V, T) + F^{\text{mag}}(V, T). \quad (1)$$

Here, the PV contribution has been ignored, and the adiabatic approximation has been used, which decouples lattice, charge, and spin degrees of freedom for thermal excitations. P is the pressure, T the temperature, V the volume, and $E_0(V)$ the total electronic energy at zero temperature, which can be directly calculated using different density functional approximations. $F^{\text{el}}(V, T)$, $F^{\text{vib}}(V, T)$, and $F^{\text{mag}}(V, T)$ are the contributions to the free energy at finite temperature from electronic, lattice, and magnetic degrees of freedom, respectively, which can be modeled based on DFT results. In this study, $E_0(V)$ was calculated using SCAN + rVV10.

Based on the electronic density of states obtained from DFT calculations (see Supplementary Fig. 1), the electronic contribution to the free energy, $F^{\text{el}}(V, T)$, can be determined by the finite temperature method⁵² according to Fermi–Dirac distribution, following the fixed density of states approximation⁵³.

The lattice vibrational contribution $F^{\text{vib}}(V, T)$ can be expressed as

$$\frac{1}{2} \sum_{q,s} \hbar \omega(q, s) + k_B T \sum_{q,s} \ln \left[1 - \exp \left(\frac{\hbar \omega(q, s)}{k_B T} \right) \right], \quad (2)$$

where $\omega(q, s)$ is the phonon frequency associated with wave vector q and band index s , and k_B is the Boltzmann constant. $\omega(q, s)$ typically depends on V and T due to the anharmonicity of the lattice potential, and it can be calculated or modeled based on DFT at different levels. The HA assumes that the lattice sees a harmonic potential at the equilibrium volume (see Fig. 1), and $\omega(q, s)$ is calculated based on the frozen-phonon approach, which computes the harmonic force constants from DFT calculations via finite atomic displacements⁵¹. The quasi-harmonic approximation (QHA) method^{51,54} takes a step further to consider the volume dependence for the phonon anharmonicity, while the temperature is assumed to indirectly affect phonon vibrational frequencies through thermal expansion. Typically, the phonon spectra of about ten or more volumes are usually required for a DFT-based QHA simulation, and such calculations are always time-consuming. Here, the QHA $F^{\text{vib}}(V, T)$ are instead approximated using the phonon density of states (see Supplementary Fig. 3) by the Debye model. The Debye temperature is then estimated based on the equation of state from DFT calculations to account for the anharmonicity^{40,41}.

We fit the static $E(V)$ curve of each phase (see Supplementary Fig. 2) to the Vinet equation of state^{40,55–58}. The total lattice vibrational contribution $F^{\text{vib}}(V, T)$ (the red curve in Fig. 2) is obtained by combining the HA (as implemented in Phonopy⁵¹) and the QHA–Debye model (as implemented in Gibbs2^{40,41}) via a scaling factor (a function of the Poisson ratio)^{59–61} to give good descriptions for both low and high-temperature ranges. The used Poisson ratios are 0.25, 0.3, and 0.3 for MnTe, Bi₂Te₃, and MnBi₂Te₄, respectively. We chose not to use the conventional QHA method⁶², not only because it is much more computationally expensive, but also because it requires more careful validation for layered systems (like GeSe⁶³) and even some conventional materials (like Si^{64,65}), in addition to the ubiquitous imaginary frequency problems^{63,66}.

An often-employed approach to capture $F^{\text{mag}}(V, T)$ of systems with localized magnetic moments starts with the effective Heisenberg Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{S}_i \hat{S}_j, \quad (3)$$

mapped from DFT calculations, with first-principles-derived exchange coefficients J_{ij} (see Supplementary Table 2 and Supplementary Fig. 4) that mediate the magnetic exchange between spins $\hat{S}$ localized at lattice sites i and j . $F^{\text{mag}}(V, T)$ can then be calculated by the eigenenergies of $\hat{H}$, similar to the previous expression for $F^{\text{vib}}(V, T)$. However, for most realistic systems, an exact analytical solution is not known. Here, $F^{\text{mag}}(V, T)$ corresponding to $\hat{H}$ is calculated using a rescaled Monte Carlo (rMC) method⁶⁷, which maps the classical Monte Carlo (CMC)-obtained thermodynamic quantities (the ALPS package⁶⁸ is used in this work) to those obtained by quantum Monte Carlo (QMC), scaled by a factor dependent on the spin quantum number

S. Although the QMC solution to $F^{\text{mag}}(V, T)$ is desired, it has a limited applicability due to the so-called (negative) sign problem^{69,70}. CMC is known to be useful and reliable for magnetic critical temperature predictions and acceptable for high temperature (above critical temperature) heat capacity predictions. At 0 K, however, CMC gives a finite heat capacity. This is incorrect, since the zero-temperature heat capacity contributed by magnons should be zero according to quantum statistics of the magnon excitations. The use of rMC corrects the low-temperature part effectively.

Explicit coupling terms, e.g., phonon–magnon, phonon–electron, and higher order phonon–phonon interactions are all assumed to be small and neglected. Formation of defects at high temperatures (such as vacancies and antisite defects¹⁴), especially for Bi_2Te_3 and MnBi_2Te_4 , may also contribute to the C_p and the free energy. This defect factor, however, is expected to largely cancel between the two phases and is possibly negligible to the total free energy. Therefore, this factor is not considered in our calculation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

Z.M. and J.S. designed the project. J.N. and J.S. proposed the frame of the computational approach, and J.N. performed the calculations. J.N., J.K., Z.M., and J.S. analyzed the data and wrote the manuscript. Y.Z., Y.G., and Y.W. took the measurement of the specific heat capacity of MnBi_2Te_4 . All authors have discussed the results.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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